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Patent Disclosure Document

DE 199 45 980 A1

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The following specifications were taken from the documents submitted by applicant.

***Polyethylene molding mass with improved ESCR stiffness relation and swelling rate,  
Method for its Manufacture and hollow bodies produced from same.***

The invention concerns a polyethylene molding mass with multi-modal mol-mass distribution, which has a total density of  $> 0.940 \text{ g/cm}^3$  and an MFI<sub>190/5</sub> in the range of 0.01 to 10 dg/min. The invention-specific molding mass contains an amount from 30 to 60 percent by weight of low-molecular ethylene-homopolymer A, which has a viscosity number  $VZ_A$  in the range from 40 to  $150 \text{ cm}^3/\text{g}$ , an amount from 30 to 65 percent by weight of high-molecular co-polymer B of ethylene and another olefin with 4 to 10 C-atoms, which has a viscosity number  $VZ_B$  in the range from 150 to  $800 \text{ cm}^3/\text{g}$ , and an amount from 1 to 30 percent by weight of ultra-high molecular ethylene-homopolymer C, which has a viscosity number  $VZ_C$  in the range from 900 to  $3000 \text{ cm}^3/\text{g}$ .

The invention also concerns a method for manufacturing the molding mass in a three-phase process and hollow bodies from the invention-specific molding mass.

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## Specification

The present invention concerns a polyethylene molding mass with multi-modal mol-mass distribution and a method for manufacturing said molding mass in the presence of a catalytic system of Ziegler catalyst and co-catalyst via a multi-step reaction sequence consisting of successive liquid phase polymerizations and hollow bodies produced from the molding mass by means of blow molding extrusion.

Polyethylene is used extensively for the production of moldings and receptacles because many moldings and receptacles require a raw material with particularly high mechanical stability, high corrosion resistance and absolutely reliable long-term constancy, said raw material likewise presenting good chemical stability and being particularly suitable for bottles, canisters and fuel tanks in motor vehicles.

EP-A-603,935 already describes a molding mass on the basis of polyethylene, which has a bi-modal mol-mass distribution and which is, among others, also suitable for the manufacture of tubing.

A raw material with a still more expanded mol-mass distribution is described in US-PS-5.338.589 and is produced with a highly active catalyst, which is known from WO 91/18934, and with respect to which the magnesium alcoholate is employed as gel-like suspension. It was determined, quite surprisingly, that the use of said raw material in moldings, in particular in tubing, facilitates simultaneous improvement in the traditionally counter-acting properties of part-crystalline thermoplastics, such as stiffness and creep tendency, on the one side and stress cracking stability and toughness, on the other side.

The known bi-modal products distinguish themselves in particular by good processing capability with concurrent excellent tension crack-stiffness relation. This property combination is of particular significance in the production of hollow bodies made of plastic, such as bottles, canisters and fuel tanks. In addition to said property combination, however, the manufacture of hollow bodies of plastic also requires a plastic melt swelling rate which is as high as possible, since the swelling rate in blow molding extrusion is directly responsible for optimal adjustment being possible with respect to wall thickness control, formation of welding seam and welding capability during production. It is known that plastics with high swelling rates with so-called Phillips-catalysts, i.e. polymerization catalysts on the basis of chromium compounds, can easily be produced. The plastics which are produced in this fashion, however, have an unfavorable tension-crack-stiffness relation in comparison with known plastics with bi-modal mol-mass distribution.

A method is known from EP-A-0 797 599 which even provides, in successive gaseous phase- and liquid phase polymerization, a polyethylene with tri-modal mol-mass distribution. And while this polyethylene is highly suitable for production of hollow bodies in blow molding extrusion plants, it is still worthy of improvement in its processing behavior because of the swelling rate of the plastic melt which is still too low.

It was the object of the present invention to develop a polyethylene molding mass by means of which, compared with all known raw materials, it is possible to realize a still better relation relative to stiffness and tension crack stability, and which, in addition, has a high melt swelling rate, which permits, during production of hollow bodies according to the blow molding extrusion method, optimal wall thickness control and, simultaneously, excellent welding seam formation and wall thickness distribution.

This object is solved by means of a molding mass of the initially mentioned type, whose typical characteristics are to be regarded in that it contains 30 to 60 percent by weight of a low-molecular ethylene-homopolymer A, 65 to 30 percent by weight of a high-molecular co-polymer B of ethylene and another olefin with 4 to 10 C atoms and 1 to 30 percent by weight of an ultra-high molecular ethylene-homo- or copolymer C, whereby all percentage specifications relate to the total weight of the molding mass.

The invention moreover concerns also a method for the preparation of said molding mass in cascaded suspension-polymerization and hollow bodies from said molding mass having excellent mechanical stability properties.

The invention-specific polyethylene molding mass has a density, at a temperature of 23°C, in the range of  $> 0.940 \text{ g/cm}^3$ , and a broad tri-modal mol-mass distribution. The high-molecular copolymer B contains minor percentages of up to 5% by weight of additional olefin-monomer units with 4 to 10 C atoms. Examples for such co-monomers are 1-butene, 1-hexene, 1-octene or 4-methylpentene-1. The ultra-high molecular ethylene-homo or -co-polymer may possibly contain an amount from 0 to 10 percent by weight of one or several of the above named co-polymers.

The invention-specific molding mass further has a melt flow index according to ASTM D 1238, expressed as  $\text{MFI}_{190/5}$  in the range from 0.01 to 10 dg/min and a viscosity number  $\text{VZ}_{\text{total}}$ , measured according to ISO/R 1191 in decalin, at a temperature of 135°C, in the range of 190 to  $700 \text{ cm}^3/\text{g}$ , preferably of 250 to  $500 \text{ cm}^3/\text{g}$ .

The tri-modality can be described as measurement for the positions of the centers of gravity of the three individual mol-mass distributions with the aid of the viscosity numbers VZ according to

ISO/R 1191, of the polymers formed in the successive polymerization steps. Attention must be paid to the following band widths of the polymers formed during the individual reaction steps:

The viscosity number  $VZ_4$  measured at the polymer following the first polymerization step is identical with the viscosity number  $VZ_A$  of the low molecular polyethylene A and lies, according to the invention, in the range from 40 to 180 cm<sup>3</sup>/g.

$VZ_B$  of the higher molecular polyethylene B formed according to the second polymerization step can be calculated according to the following mathematical formula:

$$VZ_B = \frac{VZ_2 - w_1 \cdot VZ_1}{1 - w_1}$$

whereby  $w$  represents the weight percentage of the low molecular polyethylene formed during the first phase, measured in weight percentage, in proportion to the total weight of the polyethylene with bi-modal mol-mass distribution formed during the two first phases, and  $VZ_B$  represents the viscosity number which is measured at the polymer after the second polymerization phase.

The value calculated for  $VZ_B$  normally lies in the range from 150 to 800 cm<sup>3</sup>/g.

$VZ_C$  for the ultra-high molecular homo- or co-polymer C, formed during the third polymerization phase, is calculated according to the following mathematical formula:

$$VZ_C = \frac{VZ_3 - w_2 \cdot VZ_2}{1 - w_2}$$

whereby  $w_2$  stands for the weight percentage of the polyethylene with bi-modal mol-mass distribution, formed in the two first steps, measured in percentage by weight relative to the total

weight of the polyethylene with tri-modal mol-mass distribution, formed in all three steps, and  $VZ_3$  represents the viscosity number which is measured at the polymer after the third polymerization phase and which is identical with the  $VZ_{total}$  which is already mentioned above. The value calculated for  $VZ_c$  lies, according to the invention, in the range from 900 to  $3000 \text{ cm}^3/\text{g}$ .

The polyethylene is obtained by means of polymerization of the monomers in suspension or at temperatures of 20 to  $120^\circ\text{C}$ , at a pressure in the range from 2 to 60 bar, and in the presence of a highly active Ziegler catalyst, which is comprised of a transitional metal compound and an aluminum-organic compound. Polymerization is conducted in three stages, i.e. in three successively performed stages, in suspension with an inert, saturated hydrocarbon, whereby the mol-mass is respectively regulated with the aid of dosed-in amounts of hydrogen.

The long-term activity of the polymerization catalyst which is required for the above described method is ensured by a specially developed Ziegler catalyst. A measure for the suitability of said catalyst is its extremely high responsiveness to hydrogen and its high activity remaining constant over a long period of time from 1 to 8 hours. Examples for a catalyst of this suitability are the reaction products of magnesium-alcoholates with transitory metal compounds of titanium, zirconium or vanadium and a metal-organic compound of a Group I, II or III metal of the periodic system, listed in Patent Specifications EP O 532 551, EP O 068 257 and EP O 401 776.

The invention-specific polyethylene molding mass may contain other additives aside from the polyethylene. Such additives are, for example, thermal stabilizers, anti-oxidants, UV-absorbers, light-guard screening agents, metal deactivators, peroxide destroying compounds, basic co-stabilizers in amounts from 0 to 10 percent by weight, preferably 0 to 5 percent by weight, but also fillers, reinforcing agents, softeners, lubricants, emulsifiers, pigments, optical lightening agents, flame protection agents, antistatica, propellants or combinations of these in total amounts from 0 to 50% by weight in proportion to the total weight of the mixture.

The invention-specific molding mass is particularly suitable for the manufacture of hollow bodies, such as fuel canisters, chemically resistant casks, canisters, barrels and bottles, in that the polyethylene molding mass is first plastified in an extruder at temperatures in the range from 200 to 250°C and then pressed through a nozzle into a blowing mold and there cooled off.

For processing into hollow bodies, use can be made of conventional single screw extruders with smooth inlet zone, as well as high performance extruders with finely grooved cylinders and transport-effective feeding apparatus. The screws are typically designed as decompression screws having a length from 25 to 30 D, (D = diameter). The decompression screws have a discharge zone in which temperature differences in the melt are equalized and in which shearing-action generated relaxation tensions are to be degraded.

#### Invention-specific Example 1

The polymerization of ethylene was performed by continuous method in a series of three successive reactors. The first reactor was supplied with a polymerization catalyst, sufficient suspension medium, ethylene and hydrogen. The amount of ethylene and hydrogen was adjusted in such manner, that one volume part of hydrogen corresponded to nine volume parts of ethylene.

The polymerization catalyst is composed of pro-catalyst solid matter (obtained from reaction of a magnesium-alcoholate with a transitory metal compound of titanium, circonium, vanadium and a metal-organic compound of a Group I, II or III metal of the periodic system with an inert, saturated hydrocarbon) and a co-catalyst (comprising a metal-organic compound of a Group I, II, or III metal of the periodic system).

Into the first reactor was added, by means of continuous dosing, the pro-catalyst and the co-catalyst/triethyl-aluminum, at the rate of 1/10 (mol/mol).



Polymerization in the first reactor was performed at a temperature of 76°C and a pressure of 0.78 MPa's over a time period of 3.3 hours with a hydrogen contents in the gas chamber of 67, 68 volume percent.

The suspension from the first reactor was then transferred into a second reactor in which the amount of hydrogen in the gas chamber was reduced to 16 volume parts, and the amount of C<sub>4</sub> co-monomers in the gas chamber was increased to 0.6 volume parts. Reduction of hydrogen amount took place via H<sub>2</sub>-interim pressure tension release.

Polymerization in the second reactor was performed at a temperature of 84°C and a pressure of 0.5 MPa's over a time period of 0.9 hours.

The suspension from the second reactor was transferred into the third reactor and the amount of hydrogen in the gas chamber reduced to <5 volume percent, and the amount of C<sub>4</sub>-co-monomer reduced to 0.5 vol.%.

The polymerization in the third reactor was performed at a temperature of 47°C and a pressure of < 0.23 MPa's over a time period of 0.5 hours.

The polymerization suspension leaving the third reactor is passed to granulation, after separation of suspension medium and drying step.

The viscosity numbers and volume parts applicable for w<sub>A</sub>, w<sub>B</sub>, w<sub>C</sub> of polymer A, B, C are listed in Table I, together with corresponding data for Example 2 to 4.

#### Invention-specific Example 2

Example 1 was duplicated, but included the following modifications: Polymerization in the first reactor was performed at a temperature of 82°C and a pressure of 0.89 MPa's over a time period of 2.6 hours, with a hydrogen contents in the gas chamber of 68 vol.%.

The suspension from the first reactor was then transferred into a second reactor in that the hydrogen content was reduced to 10 volume parts in the gas chamber and the amount of C<sub>4</sub>-co-monomer raised to 9.7 volume parts in the gas chamber. Reduction of hydrogen volume took place via H<sub>2</sub>-interim pressure tension release.

Polymerization in the second reactor was performed at a temperature of 80°C and a pressure of 0.37 MPa's over a time period of 1.1 hours.

The suspension from the second reactor was transferred into the third reactor and the hydrogen volume in the gas chamber reduced to 0.6 vol.% and the amount of C<sub>4</sub>-co-monomer also reduced to 0.8 vol.%.

Polymerization in the third reactor was performed at a temperature of 80°C and a pressure of 0.15 MPa's over a time period of 0.6 hours.

### Invention-specific Example 3

Example 2 was duplicated, but with the following modifications: The polymerization in the first reactor was performed at a temperature of 80°C and a pressure of 0.74 MPa's over a time period of 2.1 hours with a hydrogen contents in the gas chamber of 65 vol %.

The suspension from the first reactor was then transferred into the second reactor in that the amount of hydrogen was reduced to 4.1 volume parts in the gas chamber and the amount of C<sub>4</sub>-co-monomer in the gas chamber increased to 1.1 volume parts. The reduction of the amount of hydrogen took place by means of H<sub>2</sub>-interim pressure tension release.

Polymerization in the second reactor was performed at a temperature of 80°C and a pressure of 0.24 MPa's over a time period of 0.9 hours.

The suspension from the second reactor was transferred into the third reactor and the hydrogen amount in the gas chamber reduced to 1.1 vol. % and the amount of C<sub>4</sub>-co-monomer also reduced to 0.8 vol. %.

Polymerization in the third reactor was performed at a temperature of 60°C and a pressure of 0.12 MPa's over a time period of 0.5 hours.

#### Invention-Specific Example 4

Example 3 was duplicated, but with the following modifications: The polymerization in the first reactor was performed at a temperature of 80°C and a pressure of 0.82 MPa's over a time period of 2.2 hours with a hydrogen contents in the gas chamber of 74 vol. %.

The suspension from the first reactor was then transferred to a second reactor in that the hydrogen amount was reduced to 4.0 volume parts in the gas chamber and the amount of C<sub>4</sub>-co-monomer was raised to 1.3 volume parts in the gas chamber. The reduction of the hydrogen amount took place by means of H<sub>2</sub>-interim pressure tension release.

Polymerization in the second reactor was performed at a temperature of 80°C and a pressure of 0.20 MPa's over a time period of 0.9 hours.

The suspension from the second reactor was transferred to the third reactor and the amount of hydrogen in the gas chamber reduced to 1.0 vol. % and the amount of C<sub>4</sub>-co-monomer also reduced to 1.0 vol. %.

The polymerization in the third reactor was performed at a temperature of 60°C and a pressure of 0.08 MPa's over a time period of 0.5 hours.

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**Table 1**

<b>Example</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>VB</b>
$W_A$	0.35	0.45	0.55	0.55	0.52
$W_B$	0.55	0.45	0.35	0.35	0.48
$W_C$	0.10	0.10	0.10	0.10	0
$VZ_1 [cm^3/g]$	80	80	100	60	55
MFR(2) Powder	3.5	2.3	2.0	2.8	0.52
MFR(3) Powder	1.2	0.7	0.55	0.56	---
$VZ_{total}$ Powder	316	328	404	378	333
MFR/5 $[g/10']$ gran	1.07	0.55	0.30	0.36	0.40
MFR/21,6 $[g/10']$ gran	17.9	11	9.5	13.1	13.4
FRR 21,6/5 gran.	17	20	31.6	36.3	33.6
$VZ [cm^3/g]$ gran.	306	325	392	373	329
Density $[g/cm^3]$ gran	0.954	0.953	0.953	0.954	0.954
<b>Fracture Resistance</b>					
$0^\circ C [kJ/m^2]$	9.6	10.7	12.6	7.8	6
BKM $[N/mm^2]$	1270	1200	1240	1280	1275
SR Rheometer (%)	200	151	153	143	91
Fracture Test [h]	3.7	16	54.2	54.1/54	39

notched bar strength test<sub>iso</sub> is measured according to ISO 179. Dimensions of specimen measure 10 x 4 x 80, whereby a V- notch is made with an angle of 45°, a depth of 2 mm and a notch bottom radius of 0.25 mm.

The bending/creep module is measured according to DIN 54852-ZΔ as (?) [illegible] minute value.

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**Comparison Example**

A bi-modal product was prepared with comparable characteristic product data (MFR, density, VZ). Polymerization was performed in the first reactor at a temperature of 84°C and a pressure of 0.90 MPa's over a time period of 4.2 hours with a hydrogen contents in the gas chamber of 76 vol.%. The suspension from the first reactor was then transferred to a second reactor in which the amount of hydrogen was reduced to 3.0 volume parts in the gas chamber and the amount of C<sub>4</sub>-co-monomer in the gas chamber raised to 1.9 volume parts. Reduction of hydrogen took place by means of H<sub>2</sub>-interim pressure tension release. The polymerization in the second reactor was performed at a temperature of 83°C and a pressure of 0.21 MPa's over a time period of 1.3 hours.

**Table 2**

HK Test on Bekum BAE 3,500 ml round bottle

	1	2	3	4	VB1
Type	GX 4047				
CM-No.	949419	940431	940424	940425	
Bottom Gap	150	150	150	150	(600?)
No. or Rotation [r/min]	17.7	17.7	17.7	17.7	--
Blow Time (sec)	15	14.0	12.0	11.2	12
Weight (g)	41.4	37.4	36.0	35.6	38
Wall Thickness (mm)	1.2	1.00	0.90	0.85	--
Weld.Seam thickness (mm)	2.0	2.0	1.0	1.0	(0.5) (V-notch)
Melt Fracture [note]	2	2	2	2	2
Specks (faults)[note]	2	2	2	3	1
Comments:	lusterless	lusterless	lusterless	lusterless	lusterless

### Patent Claims

1. Polyethylene molding mass with multimodal mol-mass distribution, having a total density of  $> 0.940 \text{ g/cm}^3$  and an MFI  $_{90/5}$  in the range of 0.01 to 10 dg/min, **characterized in that** it contains an amount of 30 to 60 weight % of low-molecular ethylene-homo-polymer A, which has a viscosity number  $VZ_A$  in the range from 40 to  $150 \text{ cm}^3/\text{g}$ , an amount from 30 to 65 weight % of high-molecular co-polymer B of ethylene and an additional olefin with 4 to 10 C-atoms, which has a viscosity number  $VZ_B$  in the range from 150 to  $800 \text{ cm}^3/\text{g}$  and an amount from 1 to 30 weight % of ultra-high molecular ethylene-homo- or -co-polymer C, with a viscosity number  $VZ_C$  in the range from 900 to  $3000 \text{ cm}^3/\text{g}$ .
2. Molding mass according to Claim 1, **characterized in that** it has an outstanding ability to be processed into hollow bodies of any kind, expressed by a swelling rate in the range of 100 to 300%.
3. Method for preparation of a polyethylene molding mass according to Claim 1 or 2, according to which the polymerization of the monomers is performed in suspension at temperatures in the range from 20 to  $120^\circ\text{C}$ , at a pressure in the range from 2 to 60 bar and in the presence of a highly active Ziegler catalyst, which is comprised of a transitory metal compound and an aluminum-organic compound, **characterized in that** the polymerization is carried out in three stages, whereby the mol-mass of the polyethylene prepared in each stage is respectively regulated with the aid of hydrogen.

4. Utilization of a polyethylene molding mass according to Claim 1 or 2 for the production of hollow bodies such as fuel receptacles, canisters, barrels or bottles, whereby the polyethylene molding mass is first plasticized in an extruder at temperatures in the range from 200 to 250°C and then pressed through a nozzle into a blowing form and there cooled down.